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LOW-SHRINKAGE MIXTURES WITH QUARTZ-SERICITE-CHLORITE SHALE FOR CERAMIC TILE

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Low-shrinkage mixtures with quartz-sericite-chlorite shale for exterior and interior facing tile are studied. The tile is characterized by a high bending strength and cold resistance. The properties of the tile produced on an industrial scale meet the requirements of the standards.

The shrinkage and deformation of ceramic tile can be diminished and the operational characteristics improved by introduction of nonplastic raw components in their composition including wollastonite, diopside, and metallurgical slags [1, 2].

We studied the compositions, manufacturing process and properties of ceramic tile with quartz-sericite-chlorite shales widely encountered in nature [3] but never mentioned in publications as a component of exterior facing tile.

We prepared experimental compositions of ceramic tile from overburden rocks from the Izykhskoe coal mine, quartz-sericite-chlorite shales from the Mainskoe deposit situated in the south of the Krasnoyarsky Krai, and glass scrap. The chemical composition of the materials is presented in Table 1.

The overburden rocks are represented by argillites weathered to the state of clay. After crushing and milling, the clays are characterized by high plasticity (25 – 29), which makes it possible to introduce a leaning agent in them. The clays have a montmorillonite-kaolinite composition with an impurity of hydromica, finely disperse quartz, feldspar (anorthite), and calcium carbonates in the form of calcite and aragonite. As for the action of the temperature, the clays are intermediate between low-melting and refractory.

Chlorite-bearing shales are classified as mountain rocks that have passed the stage of metagenesis in which the initial clay minerals were transformed into micaceous lamellar formations [4].

The main phases in the shales used for ceramic mixtures are chlorite and sericite with impurities of quartz, anorthite, hydromuscovite, talc, calcite, and dolomite. It is assumed that the lamellar chlorite and sericite, as well as quartz and talc, in the shales compensate for the shrinkage phenomena in tile mixtures.

The raw mixtures were prepared and the specimens tested with the aim of using the method of rapid tile firing in conveyer furnaces. The initial components were crushed, batched, and milled in a ball mill by the wet method to a 4 – 5% residue on screen No. 005. The obtained slip was dehydrated to a moisture content of 6 – 7% and passed through a sieve with 1-mm cells. The resulting powder was used to

TABLE 1

Raw material	Mass fraction, %								
	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	Na_2O	K_2O	loss after calcination
Izykhskoe clay	61.26	16.45	0.31	4.76	4.82	1.41	0.41	0.32	9.18
Mainskoe shale	45.28	19.04	0.62	8.73	13.30	3.52	0.45	0.34	8.54
Glass scrap	67.40	5.81	–	1.86	7.21	3.48	12.83	2.00	–

TABLE 2

Component	Mass fraction, %, in composition				
	1	2	3	4	5
	Exterior facing tile				
Izykhskoe clay	100	85	75	65	60
Quartz-sericite-chlorite shales	–	7	10	15	20
Glass scrap	–	8	15	20	20
	Interior wall tile				
Izykhskoe clay	100	86	80	75	60
Quartz-sericite-chlorite shales	–	7.5	10	15	30
Glass scrap	–	6.5	10	10	10

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mold cylindrical specimens 20 mm in diameter and 20 mm high and plates 100 × 100 × 5 mm in size under a pressure of 25 MPa, dried for 30 min and roasted at 1070°C. For comparison, specimens of pure clay raw materials were fabricated by the same technology.

The physicotechnical properties of the ceramic tile were tested in accordance with the requirements of the standards for exterior facing tile and wall tile. The phase composition of the ceramic mixtures was determined by x-ray phase analysis. The compositions and properties of the tile are presented in Tables 2 and 3.

We established that the quartz-sericite-chlorite shale after milling is represented by a talc-like fatty product possessing a pronounced effect of a solid lubricant. This effect causes leveling of the normal and tangential stresses in the molded specimens, improving the quality of their surface, the precision of their edges, the deformation stability and the strength of the greenware. The greenware from pure clay exhibits numerous cracks due to nonuniform shrinkage and has low strength (4.8 MPa). With introduction of quartz- sericite-chlorite shale, microcracks in the greenware are absent and the compressive strength increases to 13.8 – 14.9 MPa.

TABLE 3

Parameter	Composition					Standard
	1	2	3	4	5	
	Exterior facing tile					
Water absorption, %	12.4	8.4	8.1	7.8	8.6	≤ 9
Shrinkage, %	1.6	0.8	0.6	0.7	0.9	–
Bending strength, MPa	10.9	18.8	17.3	16.9	17.1	–
Thermal stability, °C	130	130	130	130	130	100
Moisture expansion, %	0.1	0.026	0.03	0.021	0.029	–
Cold resistance, cycles	49	> 50	> 50	> 50	> 50	≥ 35
Green compressive strength, MPa	4.8	14.3	14.4	13.9	14.1	–
	Wall tile					
Water absorption, %	12.4	10.6	11.2	14.8	15.4	9 16
Shrinkage, %	1.6	0.6	0.2	0.1	0.2	–
Bending strength, MPa	10.9	17.6	17.1	15.8	14.6	ι 14
Thermal stability, °C	130	130	130	130	130	125 ± 5
Moisture expansion, %	0.1	0.018	0.024	0.022	0.028	–
Green compressive strength, MPa	4.8	14.9	14.6	14.4	13.8	–

* Exterior facing tile, GOST 13996–93, wall tile, GOST 6141–91.

The inconsiderable shrinkage of the tile from mixtures with shales (0.1 – 0.8%) provides for high precision of sizes and the virtual absence of bending of the face surface, which guarantees the absence of spoilage due to incorrect sizes and deformation.

Ceramic tile from mixtures with quartz-sericite-chlorite shales is characterized by low moisture expansion that does not exceed 0.03%. Since the low values of moisture expansion of the tile are associated with its high crackle resistance [4], there are grounds for expecting that tile with quartz-sericite-chlorite shale will have a quite long life.

Ceramic tile from mixtures with quartz-sericite-chlorite shales have higher bending strength and frost resistance than tile from pure clay raw materials. The cold resistance of the tile from mixtures with shale exceeds 50 cycles. Further tests for cold resistance were stopped because the attained cold resistance margin met the requirements of GOST 13996–93.

The low moisture expansion, the high strength and cold resistance are due to the phase composition of the tile after the final firing. The predominant crystalline phases are mullite, anorthite, wollastonite, and quartz.

Ceramic mixtures containing 10% quartz-sericite-chlorite shales (composition 3) were tested in the production of glazed facing tile and wall tile on the automatic line for rapid firing in the Tomsk plant of ceramic materials and products (the firing temperature is 1070°C, the time is 60 min). The properties of the resulting tile meet the requirements of the active standards and prove the experimental results (USSR Inventor's Certificate 1726440, USSR Patent 1802809).

Thus, the quartz-sericite-chlorite shales can be used to manufacture facing ceramic tile and wall tile by the method of rapid firing with low, virtually zero, shrinkage values and water absorption maintained within the admissible range. The introduction of quartz-sericite-chlorite shales in the composition of the mixtures increases the strength of the greenware and finished tile and diminishes their moisture expansion.

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